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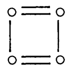
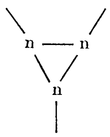
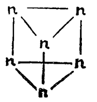
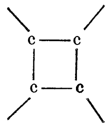
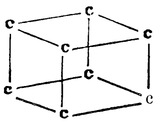
# SOME REMARKS ON A PASSAGE IN PROFESSOR SYLVESTER'S PAPER AS TO THE ATOMIC THEORY.

*Contained in a Letter addressed to the Editors by* PROFESSOR J. W. MALLET, *of the University of Virginia.*

IN the paper, published in your Journal, by Professor Sylvester on "An application of the new atomic theory to the graphical representation of the invariants and covariants of binary quantics," there occurs* a suggestion which, although parenthetic only as to the main subject of the paper, seems to deserve careful consideration and more prominence than its able author has deemed it worthy of. Professor Sylvester suggests, namely, as a modification of the atomic theory of chemists in its present form, that "leaving undisturbed the univalent atoms, every other *n*-valent atom be regarded as constituted of an *n*-ad of *trivalent* atomicules arranged along the apices of a polygon of *n* sides." Thus, using small letters to stand for the proposed "atomicules," an atom of univalent hydrogen would be graphically represented by h —, and a molecule of the same element by h — h, as at present; an atom of bivalent oxygen by $-o=o-$, and a diatomic molecule of the same by ; an atom of trivalent nitrogen by , and a diatomic molecule by ; an atom of quadrivalent carbon by , and a diatomic molecule by ; &c.

Two important advantages of this supposition are pointed out by Professor Sylvester. First, that it furnishes a conceivable explanation of the existence, in the isolated state, of single atoms of mercury, cadmium, &c.,

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* Page 78.

which may be represented as composed of two trivalent atomicules united by all three bonds, thus

$$\mathrm{hg} \equiv \mathrm{hg},$$

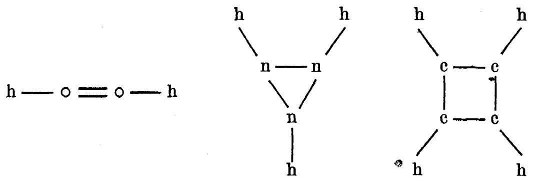
while in their ordinary compounds the same atomicules would have but two bonds *inter se*, thus

$$-\,\mathrm{hg} = \mathrm{hg}\,-\,.$$

Secondly. The explanation offered by Frankland of the variability of the valence of an atom (the weakest point in the theory of atomicity), viz., that "one or more pairs of bonds belonging to the atom of an element can unite and having saturated each other become, as it were, latent," has always seemed to me to carry with it absolutely no physical meaning—the reaction of a single and indivisible centre of chemical force *upon itself* may fairly be called "unthinkable." If, however, we admit Professor Sylvester's conception of an atom as made up of chemically inseparable but yet discrete atomicules, susceptible of force relation among themselves and to a variable extent, Frankland's idea assumes intelligible form.

To these results following from the suggested modification, I venture to add one or two others.

1°. A graphic representation is afforded of the difference between the old "equivalent weights" and the atomic weights of the elements; a difference which for many years formed the chief subject of controversy as to the atomic theory, and the chief stumbling block in the way of further progress in its application. Thus, if we take the old definition of the equivalent weight of an element, that it is "the smallest quantity of it which unites with 1 part of hydrogen," we have for oxygen 8, for nitrogen $4\frac{2}{3}$, for carbon 3, &c.; while other considerations, especially that of the fractional replacement of the hydrogen in such compounds as have yielded these figures, oblige us to assign the atomic weight 16 to oxygen, 14 to nitrogen, 12 to carbon, &c. If the following graphs be taken to represent the compounds in question—water, ammonia and marsh gas,



we see that the weight of the atom of oxygen being 16, of nitrogen 14, of carbon 12, the weight of the *atomicule* of oxygen is 8, of nitrogen $4\frac{2}{3}$, of carbon 3, &c.

2°. I venture to add still further a slight modification to the suggestion of Professor Sylvester.

So long as we regard atoms as the ultimate units of matter, we can, in the present state of our knowledge, assume nothing as to their size or shape;* indeed the greater number of chemists and physicists are perhaps rather inclined to look upon them as mere "centres of force." If, however, we consider an atom as made up of non-coincident atomicules, though these latter be but points, we may be quite ignorant of the size and shape of such a system of points, but both size and shape must clearly be predicable of it taken as a whole. And, in like manner (whether we adopt this idea of atomicules or not), molecules, made up of non-coincident atoms, must be possessed both of size and shape, whether these be by us determinable or not, and whether they be invariable or subject to change. Let it be assumed that an atom, when consisting of two or more atomicules, constitutes a *rigid* system, of invariable size and shape, the atomicules preserving permanently the same positions in relation to each other. But in a molecule made up of atoms, let it be assumed that the relative position of the atoms admits of change, and hence that in consequence of chemical combination, decomposition, substitution, &c., *distortion* of the molecules occurs, on which distortion may depend, in part at least, the changed properties of the masses made up of such molecules in aggregate.

If this idea be admitted I believe that an explanation may be found of the heat relations between the molecules of the two allotropic forms of oxygen, which possess special importance from their having the simplest connection with the atomic theory of all known cases of allotropism.

It is now generally agreed that the molecule of ordinary oxygen consists of two atoms, and that of ozone of three. The conversion of two molecules of the latter into three of the former is attended with evolution of heat, to an extent estimated by Berthelot from his calorimetric experiments at 59.200 heat units; and, conversely, an equivalent amount of extraneous energy must be exerted in the production of two ozone molecules from three of ordinary oxygen. If the usual graphs for these two bodies be employed, there is no reason apparent for the thermic relation in question; the number of bonds for each atom and the average distance between it and the other atoms with which it is connected is just the same in

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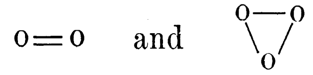
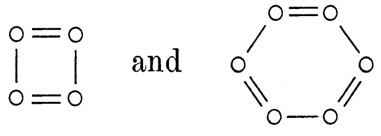
* This assertion has nothing to do with the calculations of Sir William Thomson and others as to the "size of atoms," since these calculations are only concerned with the dimensions of the *sphere of mutual interaction* of mechanical atoms or molecules, and do not at all apply to actual occupancy of space by the atoms themselves.



(ordinary oxygen.) (ozone.)

But if Professor Sylvester's graphs be substituted, namely



(ordinary oxygen.) (ozone.)

it is at once suggested to the eye* that the average distance between the atoms, as also between the atomicules, is increased in passing from the ordinary form of oxygen to ozone; or, in other words, that the production of ozone from oxygen gas is an act of *partial* chemical decomposition, not resulting in the detachment of the constituent atoms from each other, on the contrary leaving them in a state of definite chemical combination, but removed further apart than they were in the more stable form of the element—hence, as in complete, so in this which I have called partial decomposition, extraneous energy is necessary; while the reverse change, from ozone back to ordinary oxygen, is an act of more intimate chemical union, resulting in closer approximation of the constituent parts of the molecule—and hence attended with evolution of energy, as in the form of heat.

In conclusion, I would invite the attention of mathematicians to the interesting field for their examination which is being rapidly opened up by the study of the thermic changes accompanying chemical action. The researches of Thomsen and Berthelot in particular, are fast accumulating a large mass of numerical data as to heat evolved or disappearing in connection with chemical combination and decomposition, and the highest interest attaches to a proper discussion of such results in the light of the atomic theory. In too many reviews of the facts already before us there has been gross neglect even of the thermic relations of changes of physical state accompanying chemical action, but, even where these and other collateral phenomena have been duly allowed for, there has been so far no proper consideration of the force involved in the union or separation of *similar* as well as dissimilar atoms. Thus we find the formation of hydrochloric acid from its elements represented as

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* It is no valid objection to this to say that the arrangement of the four atomicules in the one case in the form of a square, and of the six in the other case as a regular hexagon, is merely imaginary, for the same result as to average distance will follow from any arrangement which is *symmetrical* (and with any assumption as to relative distances between atomicules and atoms), and dealing, as we are here, solely with *similar* atoms and atomicules we can scarcely avoid the belief that their arrangement, whatever it may be, is symmetrical.

$$H + Cl = HCl = 22.000 \text{ heat units},$$

whereas we really have

$$H_2 + Cl_2 = 2HCl = 22.000 \text{ h. u.}$$

the + 22.000 h. u. representing the algebraic sum of the thermal changes involved in the decomposition of a molecule of hydrogen (separation of its two atoms), the similar decomposition of a molecule of chlorine, and the formation of two molecules of hydrochloric acid. A mathematical discussion of the data already on hand might possibly suggest the means of so combining our calorimetric experiments as to reduce the number of unknown quantities in our equations, and lead ultimately to a clear and connected view of the force concerned in the various chemical changes which admit of being accurately examined.

UNIV. OF VIRGINIA, *July 22, 1878.*